

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11) EP 1 118 583 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication: 25.07.2001 Bulletin 2001/30

(21) Application number: 01100714.3

(22) Date of filing: 25.08.1997

(51) Int CI.7: **C01B 3/38**, C01B 3/48, B01J 8/04, B01J 8/02, H01M 8/06

(84) Designated Contracting States:

AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC

NL PT SE

(30) Priority: 26.08.1996 US 703398

(62) Document number(s) of the earlier application(s) in accordance with Art. 76 EPC: 97939541.5 / 0 922 011

(71) Applicant: Arthur D Little, Inc.
Massachusettes 02140-2390 (US)

(72) Inventors:

Clawson, Lawrence, G.
 Dover Massachusetts 02030 (US)

Mitchell, William L.
 Belmont, Massachusetts 02178 (US)

Bentley, Jeffrey M.
 Westford, Massachusetts 01886 (US)

Thijssen, Johannes HJ.
 Cambridge, Massachusetts 02140 (US)

(74) Representative:

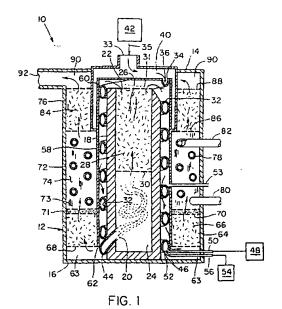
Collingwood, Anthony-Robert-et-al-McNeight & Lawrence, Regent House Heaton Lane Stockport, Cheshire SK4 1BS (GB)

Remarks:

This application was filed on 12 - 01 - 2001 as a divisional application to the application mentioned under INID code 62.

(54) Method and apparatus for converting hydrocarbon fuel into hydrogen gas and carbon dioxide

(57)An apparatus and a method are disclosed for converting hydrocarbon fuel or an alcohol into hydrogen gas and carbon dioxide. The apparatus includes a first vessel having a partial oxidation reaction zone and a separate steam reforming reaction zone that is distinct from the partial oxidation reaction zone. The first vessel has a first vessel inlet at the partial oxidation reaction zone and a first vessel outlet at the steam reforming zone. The reformer also includes a helical tube extending about the first vessel. The helical tube has a first end connected to an oxygen-containing source and a second end connected to the first vessel at the partial oxidation reaction zone. Oxygen gas from an oxygen-containing source can be directed through the helical tube to the first vessel. A second vessel having a second vessel inlet and second vessel outlet is annularly disposed about the first vessel. The helical tube is disposed between the first vessel and the second vessel and gases from the first vessel can be directed through second vessel.



Description

Background of the Invention

[0001] Fuel cells continue to play an increasingly important role in power generation for both stationary and transportation applications. A primary advantage of fuel cells is their highly efficient operation which, unlike today's heat engines, are not limited by Carnot cycle efficiency. Furthermore, fuel cells far surpass any known energy conversion device in their purity of operation. Fuel cells are chemical power sources in which electrical power is generated in a chemical reaction between a reducer (hydrogen) and an oxidizer (oxygen) which are fed to the cells at a rate proportional to the power load. Therefore, fuel cells need both oxygen and a source of hydrogen to function.

1

[0002] There are two issues which are contributing to the limited use of hydrogen gas today. Firstly, hydrogen gas (H₂) has a low volumetric energy density compared to conventional hydrocarbons, meaning that an equivalent amount of energy stored as hydrogen will take up more volume than the same amount of energy stored as a conventional hydrocarbon. Secondly, there is presently no widespread hydrogen infrastructure which could support a large number of fuel cell power systems. [0003] An attractive source of hydrogen to power fuel cells is contained in the molecular structure of various hydrocarbon and alcohol fuels. A reformer is a device that breaks down the molecules of a primary fuel to produce a hydrogen-rich gas stream capable of powering a fuel cell. Although the process for reforming hydrocarbon and alcohol fuels is established on a large industrial basis, no known analogous development has occurred for small-scale, highly integrated units.

[0004] Therefore, a need exists for a more compact apparatus for generating hydrogen gas from a variety of hydrocarbon fuel sources for use in a fuel cell to power a vehicle.

Summary of the Invention

[0005] The present invention relates to a reformer and method for converting an alcohol or hydrocarbon fuel into hydrogen gas and carbon dioxide.

[0006] According to one aspect of the invention there is provided a reformer for converting hydrocarbon fuel into hydrogen gas and carbon dioxide comprising:

 a. a first tube having a first tube inlet and a first tube outlet, the first tube inlet adapted for receiving a first mixture including oxygen-containing gas and a first fuel and the first tube outlet adapted for conducting a partially oxidized first reaction reformate into a mixing zone; and,

 b. a second tube annularly disposed about the first tube and having a second tube inlet and a second tube outlet, the second tube inlet adapted for receiving a second mixture including steam and a second fuel and the second tube outlet adapted for conducting a second reaction reformate into the mixing zone wherein the second tube is adapted for permitting steam reformation of the second mixture.

[0007] The first tube may be annularly disposed about the second tube.

[0008] The oxygen-containing gas may be air.
[0009] The second mixture may include oxygen-containing gas.

[0010] The second tube may include a first reforming catalyst.

15 [0011] The first reforming catalyst may be selected from a first group consisting of nickel, cobalt, platinum, palladium, rhodium, ruthenium, iridium and combinations thereof, and from a second group consisting of magnesia magnesium aluminate, alumina, silica, zirconia, potassium and combinations thereof.

[0012] The first fuel may be heavier by molecular weight than the second fuel.

[0013] The reformer may further comprise a fractionator communicating with the first and second tube inlets.

[0014] The reformer may further comprise a vessel annularly disposed about the second tube and defining a catalytic reforming zone, the vessel including a second reforming catalyst and adapted for receiving the first and second reaction reformates.

30 [0015] The second reforming catalyst may be selected from a first group consisting of nickel, cobalt, platinum, palladium, rhodium, ruthenium, iridium and combinations thereof and from a second group consisting of magnesia, magnesium, aluminate, silica, zirconia, potassium and combinations thereof.

[0016] The reformer may further comprise an ignition means in operable communication with the first tube.

[0017] According to a second aspect of the invention there is provided a method for converting hydrocarbon fuel into hydrogen gas and carbon dioxide within a reformer comprising the steps of:

 a. directing a first mixture of an oxygen-containing gas and a first fuel into a first tube to produce a first reaction reformate:

b. directing a second mixture of steam and a second fuel into a second tube annularly disposed about the first tube to produce a second reaction reformate:

d. transferring heat energy produced in the first tube to the second tube: and,

 e. directing the first and second reaction reformates into a reforming zone including a first reforming catalyst.

[0018] The first tube may be annularly disposed about

2

55

30

40

the second tube.

[0019] The method may further comprise the step of providing an oxygen-containing gas in the second tube. [0020] The method may further comprise the step of providing a second reforming catalyst in the second tube.

[0021] The method may further comprise the step of selecting the second reforming catalyst from a first group consisting of nickel, cobalt, platinum, palladium, rhodium, ruthenium, iridium and combinations thereof, and from a second group consisting of magnesia, magnesium aluminate, alumina, silica, zirconia, potassium and combinations thereof.

[0022] The first fuel provided may be heavier by molecular weight than the second fuel.

[0023] The method may further comprise the step of providing a fractionator for communication with the first and second tubes.

[0024] The method may further comprise the step of directing the first and second reaction reformates into a mixing zone before directing the first and second reaction reformates into the reforming zone.

[0025] The method may further comprise the step of selecting the first reforming catalyst from a first group consisting of nickel, cobalt, platinum, palladium, rhodium, ruthenium, iridium and combinations thereof and from a second group consisting of magnesia, magnesium aluminate, alumina, silica, zirconia, potassium and combinations thereof.

[0026] The method may further comprise the step of using an ignition means to ignite the first mixture in the first tube.

[0027] According to another aspect of the invention, there is provided a reformer for converting a hydrocarbon fuel into hydrogen gas and carbon dioxide comprising:

a. a first tube including a first catalyst and adapted for receiving a first mixture of steam and a first fuel:

b. a second tube annularly disposed about the first tube and adapted for receiving a second mixture of an oxygen-containing gas and a second fuel: and,

c. a third tube annularly disposed about the second tube and adapted for receiving a first reaction reformate from the first tube and a second reaction reformate from the second tube and for producing a third reaction reformate.

[0028] The first catalyst may be selected from a first group consisting of nickel, cobalt, platinum, palladium, rhodium, ruthenium, iridium and combinations thereof, and from a second group consisting of magnesia, magnesium aluminate, alumina, silica, zirconia, potassium and combinations thereof.

[0029] The first tube may have a tapered diameter.

[0030] The second fuel may be heavier by molecular

weight than the first fuel.

[0031] The reformer may further comprise a fractionator communicating with the first and second tubes.

[0032] The second tube may have a tapered diameter.

[0033] The first tube may have a first tube inlet and a first tube outlet and the second tube may have a second tube inlet and a second tube outlet, the first tube inlet having a diameter less than the first tube outlet and the second tube outlet having a diameter less than the second tube inlet.

[0034] The third tube may have a third catalyst.

[0035] The third catalyst may be selected from a first group consisting of nickel, cobalt, platinum, palladium, rhodium, ruthenium, iridium and combinations thereof, and from a second group consisting of magnesia, magnesium aluminate, alumina, silica, zirconia, potassium and combinations thereof.

[0036] The reformer may further comprise a mixing zone adapted for receiving the first reaction reformate from the first tube and the second reaction reformate from the second tube and directing the first and second reaction reformates into the third tube.

[0037] The reformer may further comprise:

a. a helical tube disposed about the third tube and having a first end communicating with an oxygen source and a second end communicating with the second tube, the helical tube adapted for receiving the second fuel at a point proximate the second end and directing the second mixture into the second tube: and,

b. a first vessel disposed about the third tube and the helical tube and adapted for directing the third reaction reformate from the third tube through the first vessel and around the helical tube.

[0038] The first vessel may further include a water inlet.

[0039] The reformer may further comprise a second vessel disposed about the first vessel and defining a shift reaction zone, the second vessel including a third catalyst.

[0040] The third catalyst may include ferric oxide and chromic oxide.

[0041] The third catalyst may include ferrous oxide and chromium oxide.

[0042] The third catalyst may be further selected from a group consisting of copper, iron, silicide, platinum, palladium and combinations thereof.

[0043] The reformer may further comprise a flow distribution region adapted for receiving the third reaction reformate from the first vessel and directing the third reaction reformate into the second vessel.

[0044] According to a further aspect of the invention there is provided a reformer for converting a hydrocarbon fuel into hydrogen gas and carbon dioxide compris-

ing:

a first vessel having a first portion defining a partial oxidation reaction zone and a first vessel inlet adapted to direct reactants including oxygen-containing gas and unburned fuel tangentially into the first portion of the first vessel: and,

a first vessel outlet disposed downstream of the partial oxidation reaction zone.

[0045] The partial oxidation reaction zone may be adapted to permit reactants to flow therethrough in a substantially helical manner in response to tangentially delivered unburned fuel.

[0046] The first vessel may include means to ignite the reactants.

[0047] The partial oxidation reaction zone may contain an open interior space without any catalyst.

[0048] The reformer may further comprise:

a helical tube disposed about the first vessel and having a first end for connection to an oxygen source and a second end for connection to the first vessel inlet, the helical tube adapted to conduct the oxygen-containing gas from the oxygen source to the first vessel: and,

a second vessel having a second vessel inlet and a second vessel outlet, the second vessel annularly disposed about the first vessel and adapted to direct product gases from the first vessel through the second vessel wherein the helical tube is interposed between the first vessel and the second vessel.

[0049] The first vessel may have a second portion disposed downstream of the first portion and defining a steam reforming reaction zone, and the first vessel outlet communicates with the steam reforming reaction zone.

[0050] The first vessel may include a perforated barrier interposed between the first and second portions.
[0051] The reformer may further comprise:

a helical tube disposed about the first vessel and having a first end for connection to an oxygen source and a second end for connection to the first vessel inlet, the helical tube adapted to conduct the oxygen-containing gas from the oxygen source to the first vessel: and,

a second vessel having a second vessel inlet and a second vessel outlet, the second vessel annularly disposed about the first vessel and adapted to direct product gases from the first vessel through the second vessel wherein the helical tube is interposed between the first vessel and the second vessel. [0052] The oxygen source may be adapted to supply air

[0053] The reformer may further comprise a conduit communicating with a water source and the second vessel and adapted to direct a supply of water to the second vessel.

[0054] The helical tube may be connected to a fuel source and may be adapted to permit fuel from the fuel source to mix with the oxygen-containing gas within a helical tube.

[0055] The helical tube may be connected to a steam source and be adapted to permit steam from the steam source to mix with the fuel and the oxygen-containing gas within the helical tube.

[0056] The steam reforming reaction zone may contain a first catalyst which may include nickel.

[0057] The reformer may further comprise a third vessel annularly disposed about the second vessel, the third vessel having a third vessel inlet and a third vessel outlet for directing product gases from the second vessel through the third vessel.

[0058] The third vessel may have a high-temperature shift reaction zone containing a second catalyst, which may include iron oxide.

[0059] The third vessel may include a cooling zone, which may contain a cooling tube having a cooling tube inlet adapted for communication with a cooling medium source and a cooling tube outlet.

[0060] The cooling medium source may be adapted to direct a liquid-phase cooling medium into the cooling tube and maintain a two-phase mixture throughout substantially an entire length of the cooling tube within the cooling zone.

[0061] The cooling tube may be helically disposed within the cooling zone.

[0062] The third vessel may have a low-temperature shift reaction zone including a third catalyst and be disposed downstream of the cooling zone.

[0063] The third catalyst may include copper.

[0064] The third vessel may have a high-temperature shift reaction zone disposed upstream of the low-temperature shift reaction zone and the cooling zone may be interposed between the high-temperature and low-temperature shift reaction zones.

[55 [0065] According to another aspect of the invention, there is provided a method for converting hydrocarbon fuel into hydrogen gas and carbon dioxide within a reformer comprising the steps of:

> a. directing a stream including an oxygen-containing gas adjacent to a first vessel to pre-heat the oxygen containing gas by heat transfer from the first vessel:

 b. introducing a stream including unburned fuel into the oxygen-containing gas stream to form a mixture including oxygen-containing gas and fuel:

50

35

40

 c. directing the mixture of oxygen-containing gas and fuel tangentially into a partial oxidation reaction zone within the first vessel: and,

d. directing the mixture of oxygen-containing gas and fuel through the partial oxidation reaction zone to produce a heated reformate stream including hydrogen gas and carbon monoxide.

[0066] The method may further comprise the step of directing the mixture of oxygen-containing gas and fuel through the partial oxidation reaction zone in a substantially helical manner.

[0067] The method may further comprise the steps of introducing into the first vessel and directing the reformate stream from the partial oxidation reaction zone to a steam reforming reaction zone including a first catalyst to produce additional hydrogen gas in the reformate stream.

[0068] The method may further include the steps of:

directing the stream including the oxygen-containing gas from an oxygen source through a helical tube interposed between the first vessel and a second vessel and into the first vessel:

directing the reformate stream from the steam reforming zone through the second vessel wherein heat energy is transferred from the reformate stream in the second vessel to the stream including oxygen-containing gas in the helical tube.

[0069] The method may further include the step of introducing water into the second vessel from a water source external to the reformer.

[0070] The method may further include the step of introducing the fuel stream and steam into the helical tube.
[0071] The method may further include the step of providing a first catalyst including nickel in the steam reforming reaction zone.

[0072] The method may further comprise the step of directing the reformate stream from the second vessel to a third vessel.

[0073] The method may further comprise the step of directing the reformate stream through a high-temperature shift reaction zone to convert a portion of the carbon monoxide of the reformate stream into carbon dioxide, wherein the high-temperature shift reaction zone includes a second catalyst and is disposed within the third vessel.

[0074] The method may further provide the step of providing a second catalyst including iron oxide in the high-temperature shift reaction zone.

[0075] The method may further comprise the step of directing the reformate stream through a cooling zone disposed in the third vessel.

[0076] The method may further comprise the steps of radially extending a plurality of fins between an inner

wall and outer wall of the third vessel, and directing a cooling medium through a cooling tube disposed within the third vessel to transfer heat from the reformate stream to the fins and to the cooling medium within the cooling tube.

[0077] The method may further comprise the step of maintaining a two-phase mixture of the cooling medium throughout substantially an entire length of the cooling tube within the cooling zone.

10 [0078] The cooling tube may be disposed in a helical manner within the cooling zone.

[0079] The method may further comprise the step of directing the reformate stream from the cooling zone to a low-temperature shift reaction zone may include third catalyst and disposed within the third vessel.

[0080] The method may further comprise the step of providing a third catalyst including copper within the low-temperature shift reaction zone.

[0081] The method may further comprise the step of directing the reformate stream though a high-temperature shift reaction zone disposed upstream of the cooling zone.

[0082] In one embodiment, the reformer includes a first vessel having a partial oxidation reaction zone and a separate steam reforming reaction zone that is distant from the partial oxidation reaction zone. The first vessel has a first vessel inlet at the partial oxidation reaction zone and a first vessel outlet at the steam reforming zone. The reformer also includes a helical tube extending about the first vessel. The helical tube has a first end connected to an oxygen-containing source and a second end connected to the first vessel at the partial oxidation reaction zone. Oxygen gas from an oxygen-containing source can be directed through the helical tube to the first vessel. A second vessel having a second vessel inlet and second vessel outlet is annularly disposed about the first vessel. The helical tube is disposed between the first vessel and the second vessel and gases from the first vessel can be directed through the second vessel.

[0083] The method includes directing oxygen-containing gas through a helical tube which is disposed around a first vessel. Hydrocarbon vapor and steam are directed into the helical tube to form a mixture of oxygen gas, fuel vapor and steam. The mixture of oxygen gas, fuel vapor and steam are directed into the first vessel. The fuel vapor spontaneously partially oxidizes to form a heated reformate stream that includes carbon monoxide, and hydrogen gas. The remaining fuel vapor is steam reformed in the heated reformate stream to form hydrogen gas and carbon monoxide. The heated reformate stream is directed over the exterior of the helical tube, whereby the heated reformate stream heats the mixture in the helical tube. A portion of the carbon monoxide gas of the reformate stream is converted to carbon dioxide and hydrogen gas by a high temperature 'shift reaction. At least a portion of the remaining carbon monoxide gas of the reformate stream is converted to carbon

40

45

dioxide and hydrogen gas by a low temperature shift reaction.

[0084] In another embodiment of a reformer for converting a hydrocarbon fuel into hydrogen gas and carbon dioxide, the apparatus includes a first tube which has a first tube inlet for receiving a first mixture of an oxygen-containing gas and a first fuel, which can be a hydrocarbon or an alcohol, and a first tube outlet for conducting a first reaction reformate of the first mixture. A second tube is annularly disposed about the first tube, wherein the second tube has a second tube inlet for receiving a second mixture of a second fuel, which can be a hydrocarbon or an alcohol, and steam. A second tube has a second tube outlet for conducting a second reaction reformate of the second mixture. A catalyst reforming zone is annularly disposed about the second tube. The first reaction reformate and the second reaction reformate can be directed through the first tube outlet and the second tube outlet, respectively, to the catalyst reforming zone for further reforming of the mixtures. In a preferred embodiment, a hydrocarbon fuel fractionator is attached at the first tube inlet and second tube inlet. The fractionator can separate a heavy portion from the hydrocarbon fuel for subsequent direction to the partial oxidation zone in the first tube. A light portion can be separated from the hydrocarbon fuel for subsequent direction to the steam reforming zone in the second tube. [0085] In another embodiment of the method for converting a hydrocarbon or alcohol fuel into hydrogen gas and carbon dioxide, a first mixture of first hydrocarbon or alcohol fuel and oxygen-containing gas is directed into a first tube. The hydrocarbon or alcohol fuel in the first mixture spontaneously partially oxidizes to form a first heated reformate stream that includes hydrogen gas and carbon monoxide. A second mixture of a second hydrocarbon or alcohol fuel and steam is directed into a second tube annularly disposed about the first tube. The second hydrocarbon or alcohol fuel of the second mixture partially steam reforms to form a second heated reformate stream that includes hydrogen gas and carbon monoxide. The first heated reformate stream and second heated reformate stream are directed through a catalyst reforming zone to further reform the reformate streams to hydrogen gas and carbon dioxide. In a preferred embodiment, the hydrocarbon fuel prior to direction into the first tube and the second tube is fractionated into heavy portion of the hydrocarbon fuel and a light portion of the hydrocarbon fuel. The heavy portion is subsequently directed to the partial oxidation zone. The light portion is directed to the steam reforming zone. [0086] This invention has many advantages. The ap-

[0086] This invention has many advantages. The apparatus can use a variety of hydrocarbon fuels, such as gasoline, JP-8, methanol and ethanol. The partial oxidation reaction zone allows the fuel to partially burn while not forming soot and while providing heat to the steam reforming zone and the other portions of the reactor annularly disposed around the partial oxidation zone. Further, the apparatus is sufficiently compact for

use in an automobile. In some embodiments, the apparatus includes a high temperature shift catalyst which allows the apparatus to be more compact and lighter in weight than if only a low temperature shift catalyst is used.

Brief Description of the Drawings

[0087] Figure 1 is an orthogonal projection side view of one embodiment of the apparatus of the present invention

[0088] Figure 2 is an orthogonal projection side view of a second embodiment of the apparatus of the present invention.

5 [0089] Figure 3 is an orthogonal projection side view of a third embodiment of the apparatus of the present invention.

Detailed Description of the Invention

[0090] The features and details of the method and apparatus of the invention will now be more particularly described with reference to the accompanying drawings and pointed out in the claims. The same numeral present in different figures represents the same item. It will be understood that the particular embodiments of the invention are shown by way of illustration and not as limitations of the invention. The principal features of this invention can be employed in various embodiments without departing from the scope of the invention. All percentages and parts are by weight unless otherwise indicated.

[0091] One embodiment of the invention is shown in Figure 1. Reformer 10 has reformer vessel 12. Reformer vessel 12 can be cylindrical in shape. Reformer 10 has upper portion 14 and lower portion 16. Disposed in the center of reformer vessel 12 is first vessel 18 which extends substantially the height of reformer vessel 12. First vessel 18 has first vessel inlet 20 for receiving gases into first vessel 18 and can tangentially direct the gases through the first vessel. First vessel 18 has first vessel outlet 22 at upper portion 14 of reformer 10 for gases to exit first vessel. Perforated plate 31 is located at first vessel outlet 22 and covers the diameter of first vessel 18. Partial oxidation reaction zone 24 is in lower portion 16 of first vessel 18.

[0092] Partial oxidation zone 24 is suitable for partial oxidation of a hydrocarbon or alcohol fuel with oxygen to form a mixture including carbon monoxide, steam and hydrogen gas. Steam reforming zone 26 is above partial oxidation zone 24 and includes a steam reforming catalyst 28. Preferably, the steam reforming catalyst includes nickel with amounts of a noble metal, such as cobalt, platinum, palladium, rhodium, ruthenium, iridium, and a support such as magnesia, magnesium aluminate, alumina, silica, zirconia, singly or in combination. Alternatively, steam reforming catalyst 28 can be a single metal, such as nickel, supported on a refractory

carrier like magnesia, magnesium aluminate, alumina, silica, or zirconia, singly or in combination, promoted by an alkali metal like potassium. Steam reforming zone 26 can autothermally reform steam and methane generated in partial oxidation zone 24 to hydrogen gas and carbon monoxide. Steam reforming catalyst 28, which can be granular, is supported within partial oxidation zone 24 by perforated plate 30 and perforated plate 31.

[0093] Helical tube 32 extends about the length of first vessel 18. First end 34 of helical tube 32 is located at inlet housing 33. Oxygen source 42 is connected to inlet housing 33 by conduit 35 with first end inlet 36 for receiving oxygen-containing gas from oxygen gas zone 40. Second end 44 of helical tube 32 is connected at first vessel inlet 20. Examples of suitable oxygen-containing gas include oxygen (O2), air, etc. Fuel inlet 46 is joined to helical tube 32 proximate to second end 44. Conduit 50 extends from fuel source 48 to fuel inlet 46. Examples of suitable fuels include hydrocarbons which encompass alcohols, also. Fuels include gasoline, kerosene, JP-8, methane, methanol and ethanol. Steam inlet 52 is proximate to fuel inlet 46. Steam can be directed from steam source 54 to steam tube 56 through first steam inlet 52 into helical tube 32. In another embodiment, fuel and steam can be directed into helical tube 32.

[0094] Second vessel 58 is annularly disposed about first vessel 18. Second vessel inlet 60 receives gaseous products from first vessel outlet 22. Second vessel outlet 62 at lower portion 16 of reformer 10 allows gas to exit second vessel 58. Helical tube 32 is disposed between first vessel 18 and second vessel 58 and gases from first vessel 18 can be directed through second vessel 58 from second vessel inlet 60 over and around helical tube 32 to second vessel outlet 62. Flow distribution region 63 conducts gas from second vessel outlet 62 to high temperature shift zone 64. Additional steam or water can be directed from a steam source into second vessel 58 through second steam inlet 53 to provide added steam to provide added cooling and further the reformation of the fuels.

[0095] High temperature shift zone 64 is annularly located between second vessel 58 and reformer vessel 12 and includes a high temperature shift catalyst. An example of a suitable high temperature shift catalyst are those that are operable at a temperature in the range of between about 300°C and about 600°C. Preferably the high temperature shift catalyst includes transition metal oxides, such as ferric oxide (Fe₂O₃) and chromic oxide (Cr₂O₃). Other types of high temperature shift catalysts include iron oxide and chromium oxide promoted with copper, iron silicide, supported platinum, supported palladium, and other supported platinum group metals, singly and in combination. High temperature shift catalyst 66 is held in place by perforated plate 68 and perforated plate 70. Gas can pass through high temperature shift zone 64 through perforated plate 70 to sulfur removal zone 71.

[0096] Above high temperature shift zone 64 is sulfur removal zone 71. Sulfur removal zone 71 includes a catalyst which can reduce the amount of hydrogen sulfide (H₂S), which is deleterious to a low temperature shift catalyst, in the gas stream to a concentration of about one part per million or less. An example of a suitable catalyst includes a zinc oxide. Sulfur removal zone 71 is sized depending on the type of fuel used. If a low sulfur fuel is used, a small sulfur removal zone is needed. If a high sulfur fuel is used, a larger sulfur removal zone is necessary. Gas can pass from sulfur removal zone 71 through perforated plate 73 to cooling zone 72.

[0097] Cooling zone 72 includes a plurality of vertical fins 74 which radiate from second vessel 58 to reformer vessel 12 which extends from high temperature shift zone 64 to low temperature shift zone 76.

[0098] Cooling tube 78 is helically disposed about second vessel 58 and is attached to vertical fins 74. Cooling tube 78 has cooling tube inlet 80 for receiving a cooling medium, such as water, through cooling tube 78 to cooling tube outlet 82. In another embodiment, cooling tube 78 is wound a second series of times around second vessel 58. The gaseous products from high temperature catalyst zone 64 can pass between the vertical fins 74 and pass over cooling tube 78 allowing gaseous products to cool.

[0099] Low temperature shift zone 76 is annularly disposed above cooling zone 78 and between second vessel 58 and reformer vessel 12 and includes low temperature shift modifying catalyst 84 for reducing carbon monoxide to a level of less than about one percent, by volume, or below. An example of a suitable low temperature modifying catalyst are those that are operable at a temperature in a range of between about 150°C and about 300°C. Preferably, the low temperature modifying catalyst includes cupric oxide (CuO) and zinc oxide (ZnO). Other types of low temperature shift catalysts include copper supported on other transition metal oxides like zirconia, zinc supported on transition metal oxides or-refractory supports like silica or alumina, supported platinum, supported rhenium, supported palladium, supported rhodium and supported gold. Low temperature shift zone catalyst 84 is held in place by lower perforated plate 86 and upper perforated plate 88. Gaseous products from cooling zone 72 can pass through perforated plate 86 through low temperature shift zone 76 through upper perforated plate 88. Exit zone 90 is above low temperature shift zone 76 and has reformer exit 92. [0100] In the method for converting hydrocarbon fuel into hydrogen gas, an oxygen-containing gas, such as air, is directed from oxygen source 42 through conduit 35 to inlet housing 33 to oxygen gas zone 40 into first end inlet 36 of helical tube 32. Reformer 10 can operate at a pressure in the range of between about 0 and 500 psig. The oxygen-containing gas, such as air, is preheated to a temperature of about 450°C. In a preferred embodiment, air has a velocity of greater than about 40 meters per second.

20

35

[0101] A suitable hydrocarbon or alcohol vapor is directed from fuel source 48 through fuel tube 50 to fuel inlet 46. Examples of suitable hydrocarbon fuels include gasoline, JP-8, methanol, ethanol, kerosene and other suitable hydrocarbons typically used in reformers. Gaseous hydrocarbons, such as methane or propane, can also be used. Steam is directed from steam source 54 through steam tube 56 to first steam inlet 52. Steam has a temperature in the range between about 100 and about 150°C. The air, steam and hydrocarbon fuel are fed at rates sufficient to mix within helical tube 32 and spontaneously partially oxidize as the mixture enters partial oxidation zone 24 through first vessel inlet 20 to form a heated reformate stream that includes carbon monoxide and hydrogen gas. In a preferred embodiment, oxygen-containing gas is tangentially directed around the interior of partial oxidation zone 24, which is an empty chamber. In partial oxidation zone 24, the reformate products can include methane, hydrogen gas, water and carbon monoxide. Partial oxidation zone 24 has a preferred temperature in the range of between about 950°C and about 1150°C. A heavier fuel is preferentially run at the higher end of the temperature range while a lighter fuel is run at a lower end of the temperature range.

[0102] From partial oxidation zone 24, reformate products are directed through perforated plate 30 to steam reforming zone 26. In steam reforming zone 26, the remaining hydrocarbon vapor in the heated reformate stream from partial oxidation zone 24 is steam reformed in the presence of steam reforming catalyst 28 into hydrogen gas and carbon monoxide. Steam reforming zone 26 typically has a temperature in the range of between about 700 and 900°C. The partial oxidation reaction provides sufficient heat to provide heat to helical tube 32 to preheat the air and other contents of helical tube 32 and also provide heat to the steam reforming step. The hydrocarbon fuel is burned partly in partial oxidation zone 24 and the remainder of the fuel with the steam is mixed with the partial oxidation zone combustion products for steam reforming and hydrocarbon shifting to carbon monoxide and hydrogen gas in the presence of steam reforming catalyst 28. The heated reformate stream exiting from steam reforming zone 26 has a temperature of between about 700°C and about 900°C. The heated reformate stream is directed between first vessel 18 and second vessel 58 and around the exterior of helical tube 32, whereby the heated reformate stream is cooled by heating the contents of helical tube 32 and also the first vessel 18 and second vessel 56.

[0103] Heated reformate stream exits second vessel outlet 62 to flow distribution zone 63, where it has been cooled to a temperature of between about 300°C and about 600°C and is directed through perforated plate 68 to high temperature shift zone 64 where essentially all of the carbon monoxide is removed or reduced by contacting the heated reformate stream with high tempera-

ture shift catalyst 66 at a temperature in the range of between about 300°C and 600°C. High-temperature shift zone 64 operates adiabatically to reduce the carbon monoxide levels with modest temperature rise. In one embodiment, heated reformate stream entering high temperature shift zone 64 has about fourteen to seventeen percent carbon monoxide, by volume, and exits high temperature shift zone 64 with about two to four percent carbon monoxide, by volume.

[0104] The high temperature shift zone treated reformate stream is directed through sulfur removal zone 71 where the hydrogen sulfide content of the stream is reduced to a concentration of less than about one part per million. From sulfur removal zone 71, the reformate is directed to cooling zone 72 where the stream contacts the vertical fins 74 and cooling tubes 78 to lower the temperature of the stream to between about 150°C and about 300°C because low temperature shift catalyst 84 is temperature sensitive and could possibly sinter at a temperature of above about 300°C. Cooling zone 72 cools high temperature reformate gas for low temperature shift zone 76. Cooling zone tubes 78 operate continuously flooded to allow accurate and maximum steam side heat transfer, to reduce fouling and corrosion to allow use of contaminated water, and to achieve a constant wall minimum temperature.

[0105] Reformate stream is directed through perforated plate 86 to low temperature shift reaction zone 76 where the reformate stream contacts low temperature shift catalyst 84 converting at least a portion of the remaining carbon monoxide gas of the reformate stream to carbon dioxide by low temperature shift reaction to form product stream. Low temperature shift reaction zone 76 operates adiabatically to reduce the remainder of the carbon monoxide to trace levels with modest catalyst temperature rise. The resulting gas product stream exits low temperature shift reaction zone 76 through perforated plate 88 to exit gas zone 90 to reformer exit 92. The exiting product stream can have a composition of about 40% hydrogen gas and less than one percent carbon monoxide on a wet volume basis.

[0106] A second embodiment of the invention is shown in Figure 2. Second reformer 100 has reformer shell 102. Reformer shell 102 has upper portion 104 and lower portion 106. Disposed in the center of reformer shell 102 is first tube 108 which extends substantially the height of reformer shell 102. First tube 108 has a first tube inlet 110 at lower portion 106 for receiving gases into first tube 108. First tube 108 is configured for receiving a first mixture of oxygen and first hydrocarbon fuel. First tube outlet 112 is configured for directing a first reaction reformate of the first mixture to mixing zone 114.

[0107] Second tube 116 is annularly disposed about first tube 108. Second tube 116 has second tube inlet 118 for receiving second hydrocarbon fuel and steam. Second tube 116 also has second tube outlet 120 for directing a second reaction reformate of a second mix-

ture. Second tube 116 can include a steam reforming catalyst. An example of a suitable catalyst includes nickel with amounts of a noble metal such as cobalt, platinum, palladium, rhodium, ruthenium, iridium, and a support such as magnesia, magnesium aluminate, alumina, silica, zirconia, singly or in combination. Alternatively, steam reforming catalyst can be a single metal, such as nickel, supported on a refractory carrier like magnesia, magnesium aluminate, alumina, silica, or zirconia, singly or in combination, promoted by an alkali metal like potassium. In another embodiment, second tube 116 can be annularly disposed within first tube 108, wherein steam and fuel can be directed into the center tube and fuel and oxygen can be directed into the tube annularly disposed around the center tube.

[0108] Oxygen source 122 is connected by oxygen tube 124 to first tube 108. An example of a suitable oxygen source is oxygen gas or air. Steam source 126 is connected to second tube 116 by steam tube 128. In one embodiment, steam source 126 can provide a source of steam at a temperature of about 150°C and a pressure of about 60 psia.

[0109] Fuel source 130 is connected by fuel tube 132 to fractionator 134. Fuel source 130 includes a suitable fuel, such as a hydrocarbon, including gasoline, JP-8, kerosene, also alcohol including methanol and ethanol. Fractionator 134 has light portion outlet 136 for directing light portion from fractionator 134 and heavy portion outlet 138 for directing heavy portion from fractionator 134. Heavy portion can be directed from heavy portion outlet 138 through heavy portion tube 140 to first tube inlet 110. Light portion can be directed from light portion outlet 138 through light portion tube 142 to second tube inlet 118. In another embodiment, separate sources can be used for heavy portion (first hydrocarbon fuel) and light portion (second hydrocarbon fuel) without having a fractionator.

[0110] Catalyst reforming zone 144 is annularly disposed about second tube 116. First reaction reformate and second reaction reformate can be directed through first tube outlet 112 and second tube outlet 120, respectively, to mixing zone 114 above catalyst reforming zone 144.

[0111] Catalyst reforming zone 144 includes a catalyst for further reforming of the mixtures to hydrogen gas. An example of a suitable catalyst includes nickel with amounts of a noble metal such as cobalt, platinum, palladium, rhodium, ruthenium, iridium, and a support such as magnesia, magnesium aluminate, alumina, silica, zirconia, singly or in combination. Alternatively, the catalyst can be a single metal, such as nickel, supported on a refractory carrier like magnesia, magnesium aluminate, alumina, silica, or zirconia, singly or in combination, promoted by an alkali metal like potassium. Catalyst reforming zone 144 can have a height that is substantially the length of first tube 108 and second tube 116. Catalyst reforming zone 144 is sufficiently porous to allow passage of gas from exit zone 146. Catalyst 147

in catalyst reforming zone 144 is held in place by lower perforated plate 148 and upper perforated plate 150. Product gases of catalyst reforming zone 144 can exit second reformer 100 from exit zone 146 through reformer shell exit 152.

[0112] In the second embodiment of the invention for converting hydrocarbon fuel into hydrogen gas and carbon dioxide, a fuel is directed from fuel source 130 to fractionator through fuel tube 132. The fuel is separated into a light portion and a heavy portion in fractionator 134. The heavy portion is directed from heavy portion outlet 138 through heavy portion tube 140 to first tube inlet 110. An oxygen-containing gas, such as air, is directed from oxygen source 122 through oxygen tube 124 to first tube inlet 110. The oxygen-containing gas and the heavy portion of the hydrocarbon fuel form a mixture in first tube, whereby the hydrocarbon fuel of the first mixture spontaneously partially oxidizes to form a first heated reformate stream that includes hydrogen gas and carbon monoxide. First heated reformate stream can be heated to about 1,525°C. The ratio of fuel to oxygen is adjusted depending upon the type of fuel used. A heavier fuel can require a higher combustion temperature. The partial oxidation of the fuel results in the fuel mixture that includes carbon monoxide, water, hydrogen gas and methane. Excess heat from the partial oxidation reaction allows transfer of heat from first tube 108 to second tube 116. By burning the heavy portion at a temperature of above about 1,375°C, there is no significant formation of carbon soot or tar in the partial oxidation zone. If necessary, ignition can be with a hot surface igniter or a spark plug.

[0113] The light portion of the fuel is directed from light portion outlet 136 of fractionator 134 through light portion tube 142 to second tube 116. Steam is directed from steam source 126 through steam tube 128 to second tube inlet 118 into second tube 116. Also oxygen gas is directed from oxygen source 122 through oxygen tube 124 to second tube inlet 118 into second tube 116. In another embodiment, only steam is directed with a light portion of hydrocarbon fuel into second tube. A second mixture of oxygen-containing gas, a light portion of hydrocarbon fuel and steam is formed in second tube 116 annularly disposed about first tube 108. Hydrocarbon fuel of second mixture partially reacts to form a second heated reformate stream that includes hydrogen gas and carbon monoxide. In the presence of steam, second mixture partially steam reforms. The heat from the reaction in first tube 108 provides energy to help cause the reaction to progress in second tube 116.

[0114] The first heated reformate stream from first tube 108 and second heated reformate stream from second tube 116 are directed through first tube outlet 112 and second tube outlet 120, respectively, into mixing zone 114. The separate tubes allow carbon reduced operation at high fuel to oxygen ratios of about four to one. It also allows using distillate fuels, such as gasoline, diesel fuel, jet fuel or kerosene, whereby heavy portion type

fuels are preferentially directed to first tube 108 for high-temperature combustion necessary to break heavy molecules while the light portion-type vapors are directed to second tube 116 for partial steam reforming as a result of thermal contact with combustion chamber. First heated reformate stream and second heated reformate stream mix within mixing zone 114. The mixture is directed from mixing zone 114 through catalyst reforming zone 144 to exit zone 146. In catalyst reforming zone 144, the remainder of the carbon monoxide is reformed to carbon dioxide to form product stream. The product stream exits through exit zone 146 and from second reformer 100 through reformer shell exit 152.

[0115] Another embodiment of the invention is shown in Figure 3. Third reformer 200 has reformer shell 202. Reformer shell 202 has upper portion 204 and lower portion 206. Disposed in the center of reformer shell 202 is first tube 208. First tube 208 has a first tube inlet 210 at lower portion 206 for receiving gases into first tube 208. First tube 208 has first tube outlet 212 at upper portion 204 for gases to exit first tube 208. First tube 208 includes steam reforming catalyst 214 for reforming a hydrocarbon in the presence of steam. An example of a suitable steam reforming catalyst is nickel with amounts of a noble metal such as cobalt, platinum, palladium, rhodium, ruthenium, iridium, and a support such as magnesia, magnesium aluminate, alumina, silica, zirconia, singly or in combination. Alternatively, steam reforming catalyst can be a single metal, such as nickel, supported on a refractory carrier like magnesia, magnesium aluminate, alumina, silica, or zirconia, singly or in combination, promoted by an alkali metal like potassium. First tube 208 is configured for receiving a mixture of steam and a first hydrocarbon or alcohol fuel. First tube outlet 212 is configured for directing a first reaction reformate of the first mixture to mixing zone 216. First tube 208 can be uniform in diameter, or alternatively, the tube can be tapered such as having a smaller diameter at first tube inlet 210 than the diameter at first tube outlet

[0116] Steam source 213 is connected to first tube 208 by steam tube 215. Steam source 213 can provide a source of steam at a temperature of about 150°C and a pressure of about 60 psia. Light fuel source 217 is connected by light fuel tube 219 to first tube 208 for directing light fuel into first tube 208. Light fuel includes a suitable fuel such as a hydrocarbon, including gasoline, JP-8, kerosene, also alcohol including methanol and ethanol. [0117] Second tube 218 is annularly disposed about first tube 208. Second tube 218 has second tube inlet 220 for receiving a mixture of oxygen and heavy hydrocarbon fuel. Second tube 218 also has second tube outlet 222 for directing a second reaction reformate of a second mixture. Second tube 218 can have a uniform diameter length of second tube 218, or alternatively second tube 218 can be tapered, such as having a larger diameter at lower portion 206 and narrower diameter at upper portion 204. Second tube outlet 222 is configured

for directing a second reaction reformate of the second mixture to mixing zone 216.

[0118] Annularly disposed about second tube is third tube 224. Third tube 224 has third tube inlet 226 proximate to mixing zone 216 for receiving a mixture of first reaction reformate of the first mixture and second reaction reformate of the second mixture. Third tube 224 has third tube outlet 228 for directing mixture of first reaction reformate and second reaction reformate from third tube 224. Third tube 224 can include steam reforming catalyst 225 for further reforming the hydrocarbon present in the mixture. An example of a suitable steam reforming catalyst includes the same catalyst described for steam reforming catalyst 214.

15 [0119] Helical tube 232 extends about the length of third tube 224. First end 234 of helical tube 232 is located at inlet housing 233. Oxygen source 242 is connected to inlet housing 233 by conduit 235 with first end inlet 236 for receiving oxygen-containing gas from oxygen gas zone 240. Second end 247 of helical tube 232 has helical tube outlet 244 for directing oxygen-containing gas into second tube 218. Examples of suitable oxygen-containing gas include oxygen (O₂), air, etc.

[0120] Heavy fuel source 241 is connected by heavy fuel tube 243 to heavy fuel inlet 246. Heavy fuel inlet 246 is joined to helical tube 232 proximate to second end 247. Examples of suitable heavy fuels include gasoline, kerosene, JP-8, methanol and ethanol. In another embodiment, the same sources of fuel can be used for heavy fuel (first hydrocarbon fuel) and light fuel (second hydrocarbon fuel). Alternatively, a fractionator, as described in Figure 2, can be used to supply a heavy fuel and a light fuel. In another embodiment, the light fuel and heavy fuel can be the same and can come from the same source.

[0121] Vessel 252 is annularly disposed about third tube 224. Vessel inlet 254 can direct reformate products from third tube outlet 228 into vessel 252. Helical tube 232 is disposed between vessel 252 and third tube 224 and gases from third tube 224 can be directed through vessel 252 from vessel inlet 254 over and around helical tube 232 to vessel outlet 256. Flow distribution region 258 conducts gas from vessel outlet 256 to catalyst reforming zone 260. Additional steam can be added through second steam inlet 257 to provide added cooling and water for reforming.

[0122] Catalyst reforming zone 260 is annularly disposed about vessel 252. Catalyst reforming zone 260 includes catalyst 262 for further shifting the reformate to hydrogen gas. An example of a suitable catalyst includes ferric oxide (Fe₂O₃) and chromic oxide (Cr₂O₃). Other types of high temperature shift catalysts include iron oxide and chromium oxide promoted with copper, iron silicide, supported platinum, supported palladium, and other supported platinum group metals, singly and in combination. The catalyst can be in powdered form and have a height substantially the height of vessel 252. Catalyst reforming zone 260 is sufficiently porous to al-

low passage of gas from flow distribution region 258 to exit zone 268. Catalyst 262 in catalyst reforming zone 260 is held in place by lower perforated plate 264 and upper perforated plate 266. Product gases of catalyst reforming zone 260 can exit third reformer 200 from exit zone 268 through reformer shell exit 270.

[0123] In a third embodiment of the invention for converting hydrocarbon or alcohol fuel into hydrogen gas and carbon dioxide, a fuel is directed from light .. fuel source 217 through light fuel tube 219 to first tube inlet 210. Steam is directed from steam source 213 through steam tube 215 to tube inlet 210 into tube 208. Light fuel partially reacts with the steam to form a first heated reformate stream that includes hydrogen gas and carbon monoxide. First heated reformate stream is directed from first tube 208 through first tube outlet 212 to mixing zone 216.

[0124] An oxygen containing gas, such as air, is directed from oxygen source 242 through conduit 235 to inlet housing 233 to oxygen gas zone 240 into first end inlet 236 of helical tube 232. The oxygen containing gas, such as air, is preheated to a temperature of about 450°C. In a preferred embodiment, the air has a velocity of greater than about 40 meters per second. As oxygen containing gas is directed through helical tube 232, a suitable heavy fuel vapor is directed from heavy fuel source 241 through heavy fuel tube 243. Examples of suitable heavy fuels include JP-8, kerosene and other hydrocarbon fuels typically used in reformers. Gaseous hydrocarbons, such as methane and propane, can also be used. The oxygen-containing gas and heavy fuel are fed at rates sufficient to mix within helical tube 232 and spontaneously partially oxidize as the mixture enters second tube 218 through second tube inlet 220 to form a heated second reformate stream that includes steam, carbon monoxide and oxygen gas. In a preferred embodiment, oxygen-containing gas is tangentially directed around the interior of second tube 218. A hydrocarbon fuel of second mixture partially reacts to form a second heated reformate stream that includes hydrogen gas and carbon monoxide. The heat in second tube 218 provides energy to cause the reaction to progress in first tube 208.

[0125] The fuel that is fed into first tube 208 and second tube 218 may or may not be about equal in amount. Second tube 218, the partial oxidation chamber, is operated at a ratio of about two to one, fuel to oxygen gas, for example, with a temperature of about 1375°C. Heat transfer from second tube 218 to first tube 208 can cause partial steam reforming in first tube 208 while the temperature is maintained at about 925°C. For liquid fuels, such as gasoline and light kerosene, the lighter fuel ends are prevaporized for delivery to first tube 208. Heavy fuels are burned in the partial oxidation zone where high temperature (about 1375°C) can break down fuel with minimal carbonization.

[0126] The first heated reformate stream from first tube 208 and second heated reformate stream from sec-

ond tube 218 are directed to first tube outlet 212 and second tube outlet 222, respectively, into mixing zone 216. The separate tubes allow carbon reduced operation at high fuel to oxygen ratios of about four or five to one, thereby reducing soot formation. It allows using distillate fuels, such as gasoline or kerosene, whereby heavy portion type fuels are preferentially directed to second tube 218 for high temperature combustion necessary to break heavy molecules while a light portiontype vapors are directed to first tube 208 for partial steam reforming as a result of thermal contact with the heated combustion from second tube 218. First., heated reformate stream and second heated reformate stream mix within mixing zone 216. The mixture is directed from mixing zone 216 through third tube inlet 226 into third tube 224.

[0127] In third tube 224, a further portion of the fuel is reformed to hydrogen and carbon monoxide to form third tube reformate stream. Third tube reformate stream exits through third tube outlet 228. Third tube reformate products are directed through vessel inlet 254 into vessel 252 where the reformate stream passes over and around helical tube 232 to vessel outlet 256. Additional steam can be added to vessel 252 through steam inlet 253 to provide additional cooling and further reform the hydrocarbon and carbon monoxide present in the reformate stream. The reformate stream is directed from flow distribution region 258 through catalyst reforming zone 260 where reformate stream is directed through catalyst reforming zone for further reforming the carbon monoxide into hydrogen gas and carbon dioxide to form product stream having a concentration of about 0.5 percent, by volume, carbon monoxide. The product stream exits through exit zone 268 through shell exit 270.

Equivalents

[0128] Those skilled in the art will recognize or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described specifically herein. Such equivalents are intended to be encompassed in the scope of the claims.

Claims

 A reformer for converting hydrocarbon fuel into hydrogen gas and carbon dioxide comprising:

a. a first tube (108) having a first tube inlet (110) and a first tube outlet (112), the first tube inlet (110) adapted for receiving a first mixture including oxygen-containing gas and a first fuel and the first tube outlet (112) adapted for conducting a partially oxidized first reaction reformate into a mixing zone (114): and,

25

30

45

50

b. a second tube (116) annularly disposed about the first tube (108) and having a second tube inlet (118) and a second tube outlet (120), the second tube inlet (118) adapted for receiving a second mixture including steam and a second fuel and the second tube outlet (120) adapted for conducting a second reaction reformate into the mixing zone (114) wherein the second tube (116) is adapted for permitting steam reformation of the second mixture.

- The reformer of claim 1 wherein the first tube (108) is annularly disposed about the second tube (116).
- The reformer of claim 1 wherein the oxygen-containing gas is air.
- The reformer of claim 1 wherein the second mixture incudes oxygen-containing gas.
- The reformer of claim 1 wherein the second tube (116) includes a first reforming catalyst.
- 6. The reformer of claim 5 wherein the first reforming catalyst is selected from a first group consisting of nickel, cobalt, platinum, palladium, rhodium, ruthenium, iridium and combinations thereof, and from a second group consisting of magnesia, magnesium aluminate, alumina, silica, zirconia, potassium and combinations thereof.
- The reformer of claim 1 wherein the first fuel is heavier by molecular weight than the second fuel.
- 8. The reformer of claim 1 further comprising a fractionator (134) communicating with the first and second tube inlets (110, 118).
- 9. The reformer of claim 1 further comprising a vessel annularly disposed about the second tube (116) and defining a catalytic reforming zone (147), the vessel including a second reforming catalyst (147) and adapted for receiving the first and second reaction reformates.
- 10. The reformer of claim 9 wherein the second reforming catalyst (147) is selected from a first group consisting of nickel, cobalt, platinum, palladium, rhodium, ruthenium, iridium and combinations thereof, and from a second group consisting of magnesia, magnesium aluminate, alumina, silica, zirconia, potassium and combinations thereof.
- The reformer of claim 1 further comprising an ignition means in operable communication with the first tube (108).
- 12. A method for converting hydrocarbon fuel into hy-

drocarbon gas and carbon dioxide within a reformer comprising the steps of:

- a. directing a first mixture of an oxygen-containing gas and a first fuel into a first tube (108) to produce a first reaction reformate:
- b. directing a second mixture of steam and a second fuel into a second tube (116) annularly disposed about the first tube (108) to produce a second reaction reformate:
- c. transferring heat energy produced in the first tube (108) to the second tube (116): and
- d. directing the first and second reaction reformates into a reforming zone (144) including a first reforming catalyst (147).
- 20 13. The method of claim 12 wherein the first tube (108) is annularly disposed about the second tube (116).
 - The method of claim 12 further comprising the step of providing an oxygen-containing gas in the second tube (116).
 - The method of claim 12 further comprising the step of providing a second reforming catalyst in the second tube (116).
 - 16. The method of claim 56 further comprising the step of selecting the second reforming catalyst from a first group consisting of nickel, cobalt, platinum, palladium, rhodium, ruthenium, iridium and combinations thereof and from a second group consisting of magnesia, magnesium aluminate, alumina, silica, zirconia, potassium and combinations thereof.
 - The method of claim 12 wherein the first fuel provided is heavier by molecular weight than the second fuel.
 - The method of claim 12 further comprising the step of providing a fractionator (134) for communication with the first and second tubes (108, 116).
 - 19. The method of claim 12 further comprising the step of directing the first and second reaction reformates into a mixing zone (114) before directing the first and second reaction reformates into the reforming zone (144).
 - 20. The method of claim 12 further comprising the step of selecting the first reforming catalyst (147) from a first group consisting of nickel, cobalt, platinum, palladium, rhodium, ruthenium, iridium and combinations thereof, and from a second group consisting of magnesia, magnesium aluminate, alumina, sili-

15

25

35

45

ca, zirconia, potassium and combinations thereof.

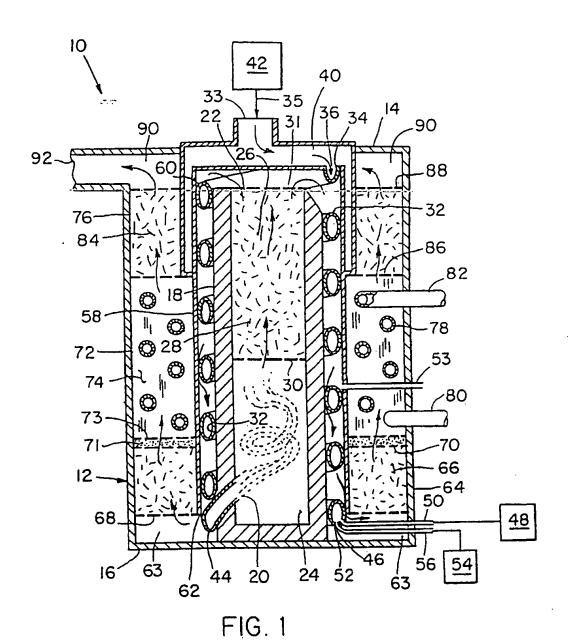
- 21. The method of claim 12 further comprising the step of using an ignition means to ignite the first mixture in the first tube (108).
- 22. A reformer for converting a hydrocarbon fuel into hydrogen gas and carbon dioxide comprising:
 - a. a first tube (208) including a first catalyst (214) and adapted for receiving a first mixture of steam and a first fuel:
 - b. a second tube (218) annularly disposed about the first tube (208) and adapted for receiving a second mixture of an oxygen-containing gas and a second fuel: and,
 - c. a third tube (224) annularly disposed about the second tube (218) and adapted for receiving a first reaction reformate from the first tube (208) and a second reaction reformate from the second tube (218) and for produoing a third reaction reformate.
- 23. The reformer of claim 22 wherein the first catalyst (214) is selected from a first group consisting of nickel, cobalt, platinum, palladium, rhodium, ruthenium, iridium and combinations thereof, and from a second group consisting of magnesia, magnesium aluminate, alumina, silica, zirconia, potassium and combinations thereof.
- 24. The reformer of claim 22 wherein the first tube (208) has a tapered diameter.
- 25. The reformer of claim 22 wherein the second fuel is heavier by molecular weight than the first fuel.
- The reformer of claim 22 further comprising a fractionator (134) communicating with the first and second tubes (208, 218).
- 27. The reformer of claim 22 wherein the second tube (218) has a tapered diameter.
- 28. The reformer of claim 27 wherein the first tube (208) has a first tube inlet (210) and a first tube outlet (212) and the second tube (218) has a second tube inlet (220) and a second tube outlet (222), the first tube inlet (210) having a diameter less than the first tube outlet (212) and the second tube outlet (222) having a diameter less than the second tube inlet (220).
- 29. The reformer of claim 22 wherein the third tube (224) has a third catalyst (225).

- 30. The reformer of claim 29 wherein the third catalyst (225) is selected from a first group consisting of nickel, cobalt, platinum, palladium, rhodium, ruthenium, iridium and combinations thereof, and from a second group consisting of magnesia, magnesium aluminate, alumina, silica, zirconia, potassium and combinations thereof.
- 31. The reformer of claim 22 further comprising a mixing zone (216) adapted for receiving the first reaction reformate from the first tube (208) and the second reaction reformate from the second tube (218) and directing the first and second reaction reformates into the third tube (224).
- 32. The reformer of claim 22 further comprising:

a. a helical tube (232) disposed about the third tube (224) and having a first end (234) communicating with an oxygen source (242) and a second end (247) communicating with the second tube (218), the helical tube (232) adapted for receiving the second fuel a point proximate the second end (247) and directing the second mixture into the second tube (218): and,

b. a first vessel (252) disposed about the third tube (224) and the helical tube (232) and adapted for directing the third reaction reformate from the third tube (224) through the first vessel (252) and around the helical tube (232).

- The reformer of claim 32 wherein the first vessel (252) further includes a water inlet (257).
- 34. The reformer of claim 32 further comprising a second vessel disposed about the first vessel (252) and defining a shift reaction zone (260), the second vessel including a third catalyst (262).
- 35. The reformer of claim 34 wherein the third catalyst (262) includes ferric oxide and chromic oxide.
- 36. The reformer of claim 34 wherein the third catalyst (262) includes ferrous oxide and chromium oxide.
- 37. The reformer of claim 36 wherein the third catalyst (262) is further selected from a group consisting of copper, iron, silicide, platinum, palladium and combinations thereof.
- 38. The reformer of claim 34 further comprising a flow distribution region (258) adapted for receiving the third reaction reformate from the first vessel and directing the third reaction reformate into the second vessel.



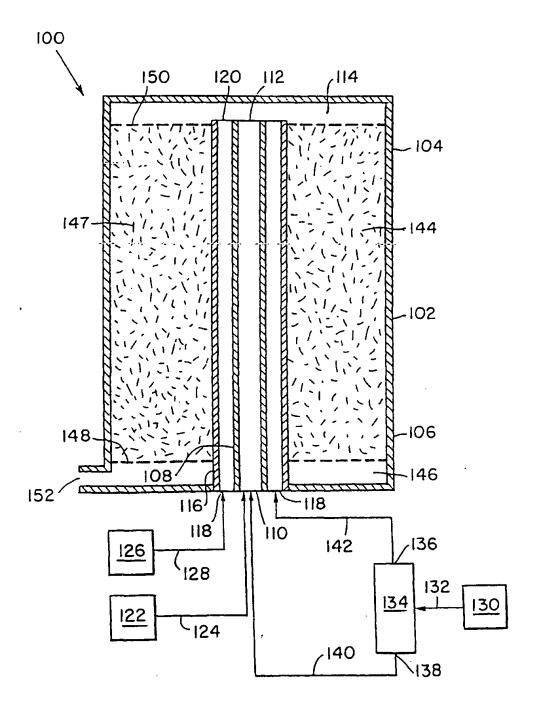


FIG. 2

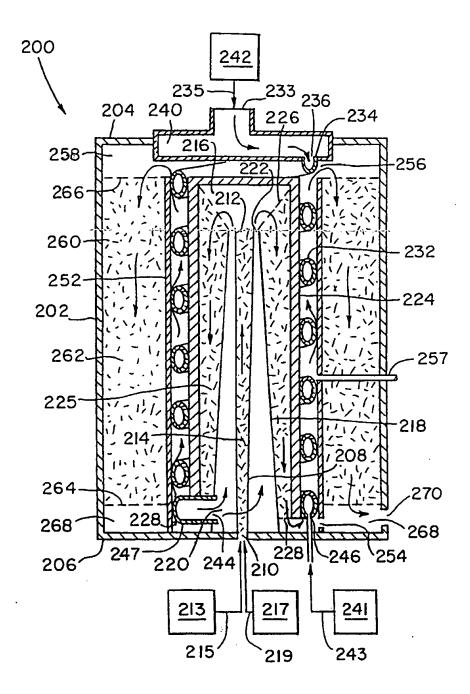


FIG. 3